Status Report: Peroxides and Formaldehyde R/V Atlantis, Spring 2010

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Species Measured

- Hydrogen Peroxide, H_2O_2
- Methylhydroperoxide, CH_3OOH
- Formaldehyde, CH_2O aka HCHO

- Photochemical significance
  - VOCs → CH_2O → CO → CO_2
  - CH_2O → HOx → O_3
  - HOx → H_2O_2 → HOx
  - CH_4 and some OVOC → CH_3OO → CH_3OOH
  - CH_3OO → CH_3OOH → CH_2O and HOx

Climate Connections
CO_2 (+1.6), CH_4 (+0.5), O_3 (+0.4) and sulfate (-0.4)

- VOCs and OVOCs → CH_2O → CO.
- CH_4 → CH_2O
  - and CH_4 → CH_3OOH.
- Peroxides and formaldehyde are directly relatable to ozone.
- Heterogeneous sulfur dioxide oxidation.

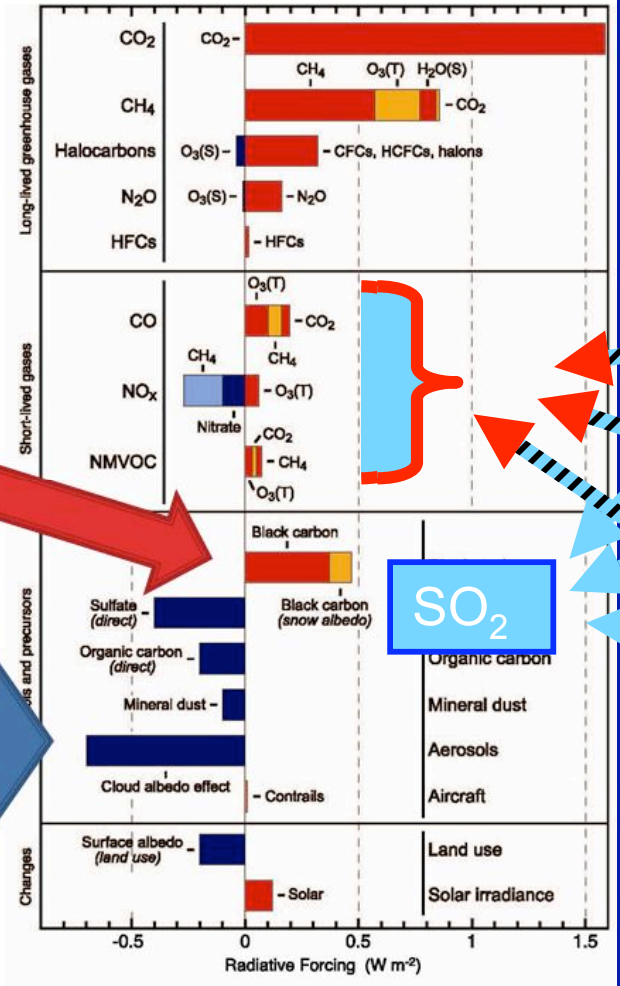
Climate Connections adapted from Ricky Rood (UMich), "blog" Weather Underground, June 2010

Global radiative forcing due to emissions of aerosols and precursors changes from 1750-2005

Black Carbon ---- Positive Radiative Forcing

Sulfate and Organic Carbon ----Negative Radiative Forcing

Cloud Albedo Effect --Negative Radiative Forcing



[IPCC, *WG1 4th Assessment Report*, 2007]

SO_2

CH_2O

CH_3OOH

H_2O_2

Formaldehyde Method - I

- Gas-to-aqueous collection
- Enzyme catalyzed derivatization
- Fluorescence product detection

- ~80% collection efficiency in CalNex
- Gas and aqueous stds.
- LN2 used for carrier gas and blanks

Formaldehyde Status

- Temporal resolution 2 minutes.
- Significant lag, ~ 25 minutes.
- LOD, 0.05 to 0.10 ppb.

- C-tainer temp effects and peroxide “cross-talk”.
  - Need to remove data under conditions of “rapid” change.
  - Need to remove data from periods of peroxide repair.

- Near final data reduction; ~ 1 month to go.

Peroxide Method - I

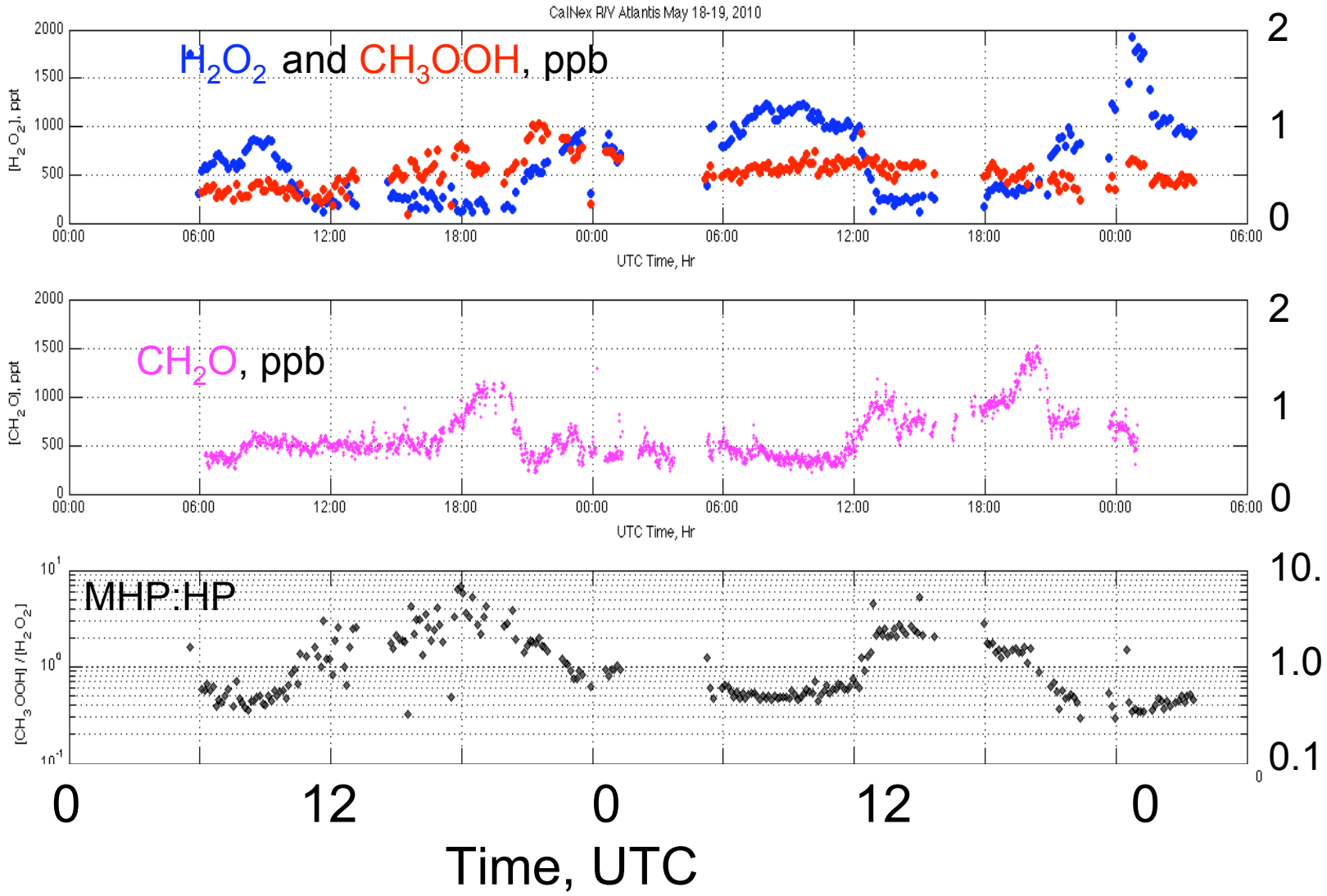
- Gas-to-aqueous collection.
- HPLC separation of hydroperoxides.
- Enzyme catalyzed derivatization.
- Fluorescence detection.

- 100 / 70% collection of H2O2 / CH3OOH.
- Gas and aqueous stds.
- LN2 used for carrier gas and blanks.

Peroxide Method - Status

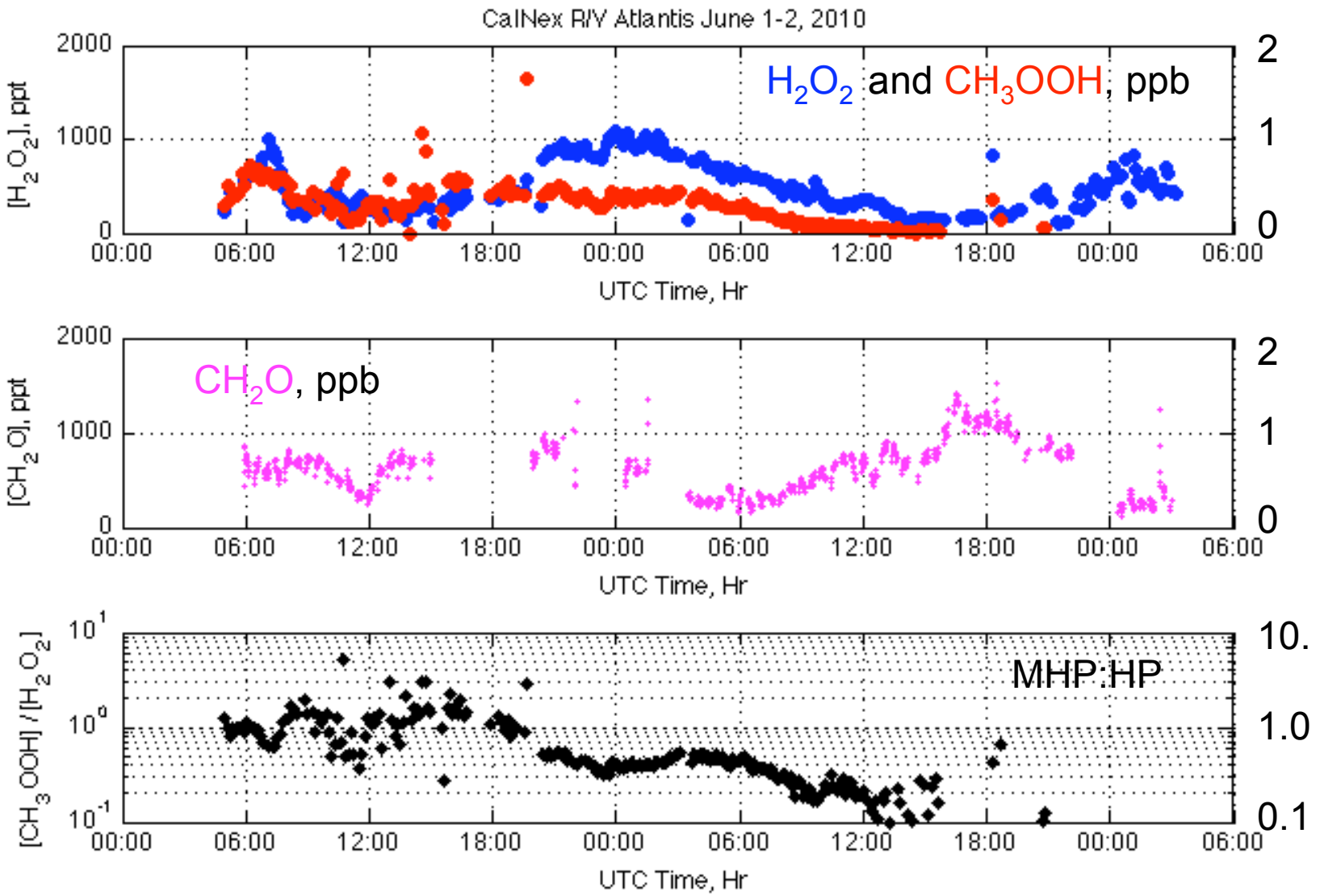
- Nearly every component failed at some point in the deployment.
- 30-sec sample every 4 minutes.
- Precision
  - H_2O_2, 0.01 to 0.05 ppb
  - CH_3OOH 0.03 to 0.1 ppb
- Hand analysis of chromatograms - time consuming.
  - Four more months to an archival product.

Example Data: 5/18-19/2010



Los Angeles Region

Example Data June 1-2, 2010



Monterey to San Francisco Bays

Summary

- Formaldehyde data in ~1 month.
- Peroxide data in ~4 months.
- Dynamic photochemical interplay between peroxides and between peroxides and formaldehyde.
- Will examine BL height, cloud and ocean surface and hydrogen peroxide.

It’s a small world at times; sometimes even smaller.